



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :  D21C 11/12, 11/00		A1	(11) International Publication Number: WO 97/23687  (43) International Publication Date: 3 July 1997 (03.07.97)		
(21) International Application Number: PCT/US96/19091  (22) International Filing Date: 29 November 1996 (29.11.96)		(81) Designated States: AU, BR, CA, CN, FI, JP, MX, NO, NZ, VN, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).			
(30) Priority Data: 08/577,850 22 December 1995 (22.12.95) US		Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>			
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(54) Title: BLACK LIQUOR GASIFICATION PROCESS AND REGENERATION OF PULPING LIQUOR					
(57) Abstract					
<p>The black liquor (10) from a kraft pulping process is gasified in a fluidized bed reactor (12) in the presence of solid calcium compounds (CaO, CaCO<sub>3</sub>, Ca(OH)<sub>2</sub>) which react with the sulfur compounds (H<sub>2</sub>S, COS) to produce solid CaS. The solid CaS along with the other primary solids (Na<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>S) are removed (18) from the reactor (12) and processed to form one or more white liquor streams for recycle to the pulping process. In this processing, the Na<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>S are dissolved (72) to form green liquor and the CaS is reacted (78) with NaOH to form NaHS. The causticizing of the green liquor may be separate from or combined with the conversion of the CaS in the green liquor to form a single white liquor stream (104) or the CaS may be separated from the green liquor and processed entirely separately to form a second high sulfide white liquor stream (174).</p>					

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## Black Liquor Gasification Process And Regeneration Of Pulping Liquor

### Background of the Invention

This invention relates to a system and process for the processing of the spent pulping liquor from a kraft pulping process, known as black liquor, to recover the chemicals and produce fresh pulping liquor. More specifically, the system and process involve black liquor gasification in a fluidized bed reactor to produce a product gas and a dry solids product, without the formation of any smelt, and then the recovery of the chemicals to produce fresh pulping liquor streams with controlled compositions.

The kraft pulping process employs an alkaline pulping liquor, known as white liquor, to react with the lignins in the wood and free the fibrous portions. Following a series of filtering and washing steps, the fibrous portion is separated as raw pulp and the remaining spent cooking liquor, which is dark in color, is known as weak black liquor. This liquor, which is approximately 85% water, is then subjected to a series of various types of evaporation to produce strong black liquor with solids content greater than 50%. The strong black liquor is then ready for the chemical recover phase.

The typical prior art process for treating black liquor to recover chemicals employs what is commonly referred to as a chemical recovery furnace. In these furnaces, which are operated as boilers for the generation of steam, the strong black liquor is fired to burn the organic content and to form a smelt composed primarily of sodium sulfide and sodium carbonate. This smelt is drained from the smelt bed in the bottom of the furnace, dissolved in water to form green liquor and then causticized to form the white pulping liquor containing sodium sulfide and sodium hydroxide.

U.S. Patent 5,284,550 entitled "Black Liquor Gasification Process Operating At Low Pressure Using A Circulating Fluidized Bed," which issued February 8, 1994 and U.S. Patent 5,425,850 entitled "CFB Black Liquor Gasification System Operating At Low Pressures," which issued 5 June 20, 1995 and which are both assigned to the same assignee as the present application, describe and claim one such system and process for replacing a chemical recovery furnace. Referring to the subject matter of U.S. Patents 5,284,550 and 5,425,850, they basically involve the replacement of the chemical recovery furnace with 10 a black liquor gasification system using a circulating fluidized bed reactor arrangement including the arrangement for processing the gases and solids which are produced to generate fresh cooking liquor. In the processes disclosed in these prior patents, kraft black liquor is gasified under substoichiometric conditions to form a product gas rich in sulfide, 15 primarily H<sub>2</sub>S with some COS, and a solid bottoms product containing primarily Na<sub>2</sub>CO<sub>3</sub> along with some unreacted Na<sub>2</sub>SO<sub>4</sub> and some Na<sub>2</sub>S. The bottoms product is dissolved to form what is referred to as green liquor which is then reacted to convert the Na<sub>2</sub>CO<sub>3</sub> to NaOH. This is done by a causticizing process where slaked lime, Ca(OH)<sub>2</sub>, is added to 20 convert the Na<sub>2</sub>CO<sub>3</sub> to NaOH and CaCO<sub>3</sub>. The solid CaCO<sub>3</sub> is then calcined in a kiln to convert it to CaO which is then slaked and recycled to the causticizer. The resulting liquor is referred to as white liquor with a high sodium content and is recycled to the digester. The sulfur-rich 25 product gas is separately processed in a reactor or scrubber to recover the sulfur compounds usually as Na<sub>2</sub>S. This sulfur recovery from the product gas may be carried out by wet scrubbing with NaOH and/or Na<sub>2</sub>CO<sub>3</sub> or it may be by dry scrubbing with calcium compounds (CaO, Ca(OH)<sub>2</sub>). In any case, the sulfur in the product gas (H<sub>2</sub>S, COS) is converted to high sulfide white liquor containing Na<sub>2</sub>S and/or NaHS.

### Summary of the Invention

The invention involves the gasification of black liquor in a fluidized bed reactor to recover both sodium and sulfur for use in the kraft pulping process. The system will produce solid sodium and solid sulfur compounds in the gasifier suitable for conversion into kraft white liquor. Specifically, the invention employs a calcium reactant which is added to the gasifier to react with the sulfur compounds ( $H_2S$  and  $COS$ ) directly in the gasifier rather than in a separate scrubber/reactor. The calcium reactant may be  $CaO$ ,  $CaCO_3$  or  $Ca(OH)_2$  including materials which contain these reactants such as limestone and dolomite. The presence of the calcium compounds allows sulfur to be captured in the gasifier at the same time pyrolysis of black liquor occurs. Sulfur reacts with calcium ( $CaO$ ,  $CaCO_3$  or  $Ca(OH)_2$ ) to form solid calcium sulfide. The solids from the gasifier containing  $Na_2CO_3$ ,  $Na_2S$  and  $CaS$ , as well as some unreacted calcium compounds, are drained from the gasifier for conversion into kraft pulping liquor. The sodium compounds ( $Na_2CO_3$  and  $Na_2S$ ) are dissolved to form green liquor containing undissolved calcium compounds. The sodium carbonate is converted to  $NaOH$  through standard causticization. Calcium sulfide is converted to sodium hydrosulfide ( $NaHS$ ) by reaction with sodium hydroxide ( $NaOH$ ). These processes produce a white liquor suitable for use in kraft pulping.

### Brief Description of the Drawings

Figure 1 is a process flow diagram of a black liquor gasification system according to the prior art.

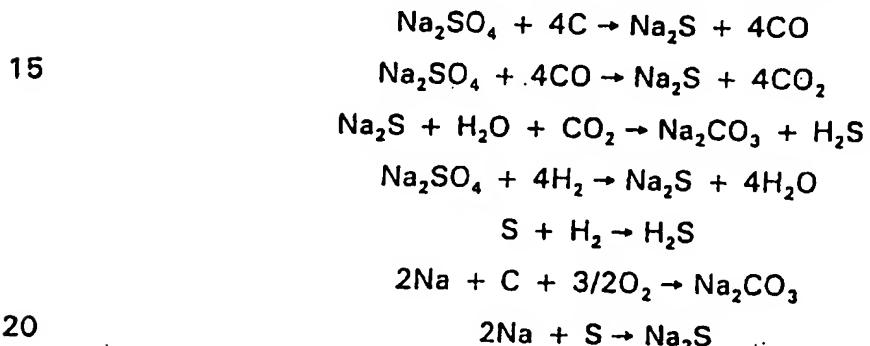
Figure 2 is a process flow diagram illustrating a black liquor gasification system incorporating the present invention.

Figure 3 is a process flow diagram similar to Figure 2 but modified for the combined conversion of  $CaS$  and  $Na_2CO_3$ .

Figure 4 is a process flow diagram illustrating a black liquor gasification system according to the present invention modified to provide multiple white liquor streams with variable sulfidity levels.

#### Description of the Preferred Embodiment

5       Figure 1 is a representation of the process flow diagram for a black liquor gasification system as described in the previously mentioned prior U.S. Patents 5,284,550 and 5,425,850. Strong black liquor 10 derived from the pulp digestion process is fed to the circulating fluidized bed gasifier 12. Fluidizing air 14 and reaction air 16  
 10      are also fed into the gasifier 12 as explained by the two prior patents previously identified. The gasification process is carried out with substoichiometric oxygen levels and the primary net reactions with respect to sodium and sulfur which occur in the gasifier are as follows:



The total air to the gasifier is generally in the range of 20% to 50% of stoichiometric which results in the gasification of more than 60% and up to 99% of the sulfur contained in the black liquor. The remaining sulfur reacts with sodium to form  $\text{Na}_2\text{S}$  which remains a solid  
 25      and is discharged out the bottom along with the  $\text{Na}_2\text{CO}_3$  and any unreacted  $\text{Na}_2\text{SO}_4$ . The solids which are formed, primarily  $\text{Na}_2\text{CO}_3$ , are collected and drained from the bottom of the gasifier as bottoms solids stream 18 while the gas product 20 is removed from the top of the gasifier 12. The gas stream 20 contains sulfur, primarily as  $\text{H}_2\text{S}$ , in

addition to the other products of the substoichiometric oxidation process, namely CO<sub>2</sub>, CO, H<sub>2</sub>, H<sub>2</sub>O and N<sub>2</sub>.

The bottoms stream 18 from the gasifier 12, which is a solids stream containing primarily Na<sub>2</sub>CO<sub>3</sub> but with some small amount of Na<sub>2</sub>S, is fed to the dissolving tank 22. The sodium solids are dissolved in a liquid stream 24 which may be water or a weak liquor or scrubber liquor stream to form green liquor. In any event, the sodium sulfide content of the selected dissolving liquid 24 is low. The resulting green liquor stream 26 contains more than 70% and up to 95% sodium as sodium carbonate on a mole basis.

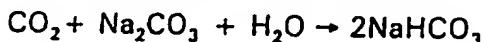
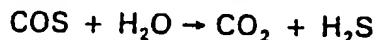
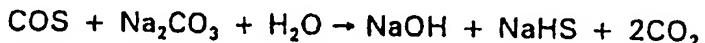
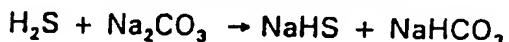
The green liquor stream 26 is fed to the causticizer 28 where slaked lime, Ca(OH)<sub>2</sub>, is added from line 30 to convert the Na<sub>2</sub>CO<sub>3</sub> to NaOH and CaCO<sub>3</sub>. The slurry 32 from the causticizer 28 is fed to the settling tank 34 where the solids, primarily CaCO<sub>3</sub>, are separated out as a sludge 36 leaving the low sulfide white liquor stream 38. The CaCO<sub>3</sub> sludge 36 is washed with water in the mud washer 40 leaving a weak wash stream 42 which can be used in the plant, as needed. The washed CaCO<sub>3</sub> 44 is fed to the kiln 46 for calcining to CaO and then to the slaker 48 for conversion back to Ca(OH)<sub>2</sub>. The white liquor stream 38 is composed mainly of NaOH with small amounts of Na<sub>2</sub>S and is recycled to the digester.

The gas product 20 from the gasifier 12 would first be cleaned of entrained particulate material at 50 by some form of mechanical separator such as a cyclone with the removed solids being recycled at 52 back to the gasifier. The remaining gas stream from the solids separator means 50 may be cooled at 54 down to the saturation temperature via recovery of heat. If any additional fine dust removal is needed, the gas would then be sent through an electrostatic precipitator, bag filter or some other form of dust removal equipment (not shown). For further details of the mechanical separation, cooling

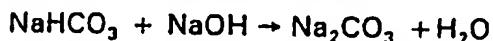
and dust removal, see the previously mentioned prior patents 5,284,550 and 5,425,850.

The cleaned and cooled gas product stream 56 is fed to the sulfur recovery scrubber 58. The scrubber 58, which operates in a known manner, employs a liquor stream 60 containing sodium values ( $\text{Na}_2\text{CO}_3$  and  $\text{NaOH}$ ) to react with the sulfur compounds, primarily  $\text{H}_2\text{S}$  with some  $\text{COS}$ , to form a liquor stream 62. Regarding the scrubbing liquor stream 60, it may in fact be several different liquor streams from various sources in the plant. The primary reactions which take place in the scrubber 58 are as follows:

Absorption Reactions



Neutralization Reaction



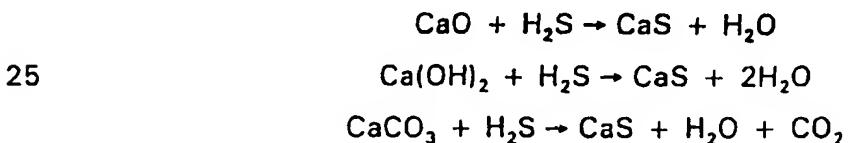
The clean overhead gas 64 from the scrubber 58 now contains primarily  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_4$  and  $\text{N}_2$ . There is sufficient heating value in this gas stream 64 so it is typically burned in combustion equipment such as a steam generator or lime kiln. The liquor stream 62 from the scrubber 58 contains primarily  $\text{Na}_2\text{S}$  with smaller amounts of  $\text{Na}_2\text{CO}_3$ . This green liquor stream 62 is fed to a holding tank 66 from which it is used to prepare a high sulfide white liquor stream which will typically involve another causticizing operation for the  $\text{Na}_2\text{CO}_3$ .

The present invention improves upon the prior art system of Figure 1 which has just been described in that it provides for the capture of the sulfur in the gasifier and eliminates the requirement for a scrubber/reactor to remove the sulfur from the gases. In the present invention, the gasifier is operated with a bed of particles consisting of

those described in the prior art plus one or more calcium compounds, CaO, Ca(OH)<sub>2</sub> and/or CaCO<sub>3</sub>, which react with the sulfur compounds to form CaS.

Referring to Figure 2, the present invention has the same basic arrangement of a circulating fluidized bed gasifier 12 fed with black liquor 10 and fluidizing and combustion air 14 and 16. A similar overhead gas stream 20 is produced and the solids are separated at 50 and recycled back to the gasifier in line 52. This line 52 would actually comprise a conventional solids return system consisting of a discharge duct from the bottom of the separator 50 and a fluidization seal system, known as a G valve or a seal pot. This is to assure one way flow of solids from the separator 50 back to the gasifier. The remaining gas stream 56 will be discussed hereinafter.

The operation of the gasifier in the present invention, as shown in Figure 2, differs from the prior art gasifiers, such as shown in Figure 1, in that calcium compounds are introduced into the gasifier through line 68. The calcium compounds in line 68 comprise recycled calcium compounds and make-up calcium compounds added as needed at 70. The source of the recycle calcium compounds will be apparent from the further description. In the gasifier, the relevant reactions involving the calcium, sodium and sulfur at the substoichiometric, reducing conditions include the gasifier reactions previously indicated plus the following reactions involving the added calcium compounds:



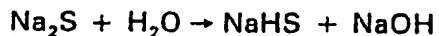
The CO<sub>2</sub> and water vapor which are formed exit with the gas from the top of the gasifier while almost all of the solid compounds which are circulated in the gas stream 20 are separated at 50 and returned to the gasifier 12. Ultimately, the solid compounds exit out of the bottom of the gasifier at 18. The solid product from the gasifier

contains primarily  $\text{Na}_2\text{CO}_3$ ,  $\text{Na}_2\text{S}$ ,  $\text{CaS}$  and any unreacted  $\text{Na}_2\text{SO}_4$ ,  $\text{CaO}$  and  $\text{CaCO}_3$ .

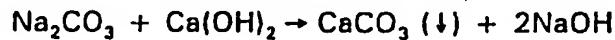
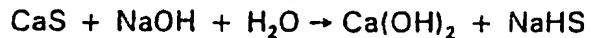
The gasifier must be operated in a temperature range where the solids do not melt and agglomerate. Some solid compounds formed in the normal course of black liquor pyrolysis, such as certain sodium and potassium salts, tend to melt at temperatures as low as 500°C to 600°C. The sodium and potassium salts also react with higher melting sodium compounds,  $\text{Na}_2\text{CO}_3$  (851°C) and  $\text{Na}_2\text{S}$  (1180°C), to form eutectics which lower the bed melting temperature. Such reactions tend to reduce the allowable operating temperature of the gasifier. Generally the gasifier will operate between 650°C and 850°C and most likely between 700°C - 750°C. However, with the circulating solids that includes calcium compounds, the gasifier may be operated at higher temperatures. The presence of the dry, high melting point calcium compounds will counter the agglomerating effect that the melting of other, lower melting solids would have on the fluidization characteristics. First, the dry calcium compounds will bind to and coat any melted compounds so that they will not agglomerate. Second, there will be a dilution of any melted compounds by the dry calcium compounds, so that any agglomeration will be insignificant and will not cause the collapse of the fluidized bed. Third, there may be reactions (unknown) which mitigate the formation of eutectics and raise the bed melting temperature. The advantage of being able to operate the gasifier at a higher temperature is that the reactions involved will proceed at a higher rate. Also, the high temperatures result in high absorption rates of sulfur. Sulfur absorption up to 99% or more may be achieved in the range of 700 to 900°C.

The solids stream 18 from the gasifier is fed to the dissolving tank 72. Water, either as make-up water 74 or the weak wash return stream 76, is added to the tank 72 where the  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{S}$  are dissolved to form green liquor containing solid  $\text{CaS}$ ,  $\text{CaO}$ ,  $\text{CaCO}_3$  and

inert compounds originating from the black liquor. These inert compounds are referred to as ash or non-process elements (NPEs). The CaO hydrates with the water to form  $\text{Ca}(\text{OH})_2$ . Sodium sulfide hydrolyzes to form two compounds consisting of sodium hydrosulfide 5 (NaHS) and sodium hydroxide (NaOH). The reactions are as follows:



The liquor stream 78 is fed to a reaction tank 80 to convert the sulfur in CaS into NaHS. White liquor 82 is fed to the tank where the 10 active compound, sodium hydroxide (NaOH), reacts with CaS to form NaHS and calcium hydroxide  $\text{Ca}(\text{OH})_2$ . The main reactions occurring during CaS conversion are as follows:



15 These reactions are time and temperature sensitive. The greatest conversion occurs at temperatures above 80°C. NaOH is required to convert CaS to NaHS and the  $\text{Ca}(\text{OH})_2$  is required for the conversion of  $\text{Na}_2\text{CO}_3$  to NaOH. These reactions complement each other and help minimize the addition of NaOH. Since  $\text{Na}_2\text{CO}_3$  is far more 20 abundant than CaS, the balance of the  $\text{Na}_2\text{CO}_3$  is converted in a conventional causticizer.

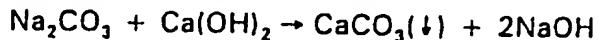
The effluent green liquor 84 from the CaS conversion at 80 now contains NaOH and NaHS as dissolved compounds plus  $\text{CaCO}_3$ , unreacted  $\text{Ca}(\text{OH})_2$  and the non-process elements as suspended solids.

25 The green liquor is fed to a solids separation device 86 to clarify the green liquor. Clarified green liquor 88 is discharged and sent to causticizer 90 for final conversion into white liquor.

30 Solids 92 from filter 86 are washed at 94 with water 96 to remove residual sodium compounds and the solids 98 are returned to the gasifier. The liquid 76 separated from the solids is returned to the dissolving tank 72. The solids 94 returned to the gasifier will contain

non-process elements that flow through the chemical recovery process as inert material. The non-process elements which are contained in the black liquor will build up to high levels if not removed. In order to maintain a low level of non-process elements, the solids stream can be 5 purged at 100 or filtered to maintain the desired level. Make-up calcium 70 will be introduced as required to achieve the required calcium content to the gasifier 12.

The final conversion process to form white liquor occurs in the causticizer 90. Slaked lime ( $\text{Ca}(\text{OH})_2$ ) 102 is fed into the causticizer 10 which converts  $\text{Na}_2\text{CO}_3$  to  $\text{NaOH}$  by the following equation:



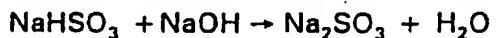
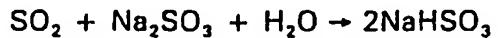
Unclarified white liquor 104 is discharged from the causticizer 90 and sent to a filter 106 to remove the calcium solids. Clarified white liquor 108 is then sent to the digester for pulping of wood. Some white liquor 82 is diverted to the CaS conversion process as previously 15 explained.

Calcium carbonate, which is the primary solid 110 removed from white liquor, is processed through conventional calcining and slaking processes. The  $\text{CaCO}_3$  is first washed with water 112 and dewatered 20 in the filter 114. The dewatered  $\text{CaCO}_3$  116 is calcined in a lime kiln 118 to produce lime ( $\text{CaO}$ ) 120 which is slaked at 122 with water 124 to form the calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) 102 for use in the causticizer 90. Liquid 126 taken from the washer 114 may be returned to the dissolving tank 72 or the causticizer 90 as desired.

25 The clean overhead gas 56 from the separator 50 now contains primarily  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_4$  and  $\text{N}_2$  and probably some small quantity of unreacted  $\text{H}_2\text{S}$  and  $\text{COS}$ . There is sufficient heating value in this gas stream 56 so it is burned in the combustion equipment 128 which, for example, could be a steam generator or the lime kiln 118.

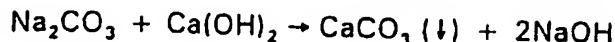
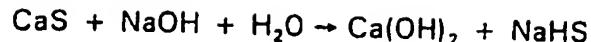
30 The flue gas stream 130 from the combustion equipment 128 is cleaned at 132 to remove any remaining entrained particulate solids which are

recycled at 134 to the gasifier 12 or sent to disposal. The cleaner 132 may be a hot gas filter, a baghouse, an electrostatic precipitation or a wet scrubber. Because there is not 100% H<sub>2</sub>S removal in the gasifier 12 and the gas stream 56 contains low concentrations of H<sub>2</sub>S which 5 will be oxidized to SO<sub>2</sub> in the combustion equipment 128, the flue gas stream 136 from the cleaner 132 contains some SO<sub>2</sub> which can be vented to the atmosphere if the SO<sub>2</sub> level is low enough or the flue gas can be scrubbed at 138. A scrubbing solution 140, such as a NaOH 10 solution, will convert the SO<sub>2</sub> to Na<sub>2</sub>SO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub>. The resulting scrubbing effluent 142 containing the sulfite and sulfate compounds, both of which can be used in pulping, is then returned to the digestion cycle. Production of sodium sulfite can be controlled with the black liquor gasification process by controlling the proportion of sulfur which is gasified as H<sub>2</sub>S and other reduced sulfur compounds. This is 15 accomplished by controlling the mole ratio of calcium to sulfur in the reactor. The inclusion of this scrubber 138 reduces the total sulfur emissions from the plant and conserves sulfur for use in the process. The remaining gases 139 from the scrubber 138 may usually be discharged to the atmosphere. The reactions which take place in the 20 SO<sub>2</sub> scrubber 138 are as follows:



If desired, the cleaner 132 may precede the combustion equipment 25 128.

Figure 3 represents a modified version of the process described in reference to Figure 2 in which both CaS and Na<sub>2</sub>CO<sub>3</sub> are converted together. Green liquor 78 containing calcium solids and non-process elements are fed to a conversion process 144 in which the sulfur as 30 CaS is converted to NaHS and the sodium as Na<sub>2</sub>CO<sub>3</sub> is converted to NaOH by the following equations:



The resulting unclarified white liquor 146 containing calcium solids and non-process elements are filtered at 148 to generate clarified white

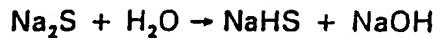
5 liquor 150 and solids 152. The solids 152 are washed with water 154 in the washer/filter 156 producing a solids stream 158 primarily of  $\text{CaCO}_3$  and a liquid stream 160. The liquid wash stream 160 is returned to the dissolving tank 72 along with whatever additional water may be required.

10 A standard lime kiln 161 and slaker 162 system regenerates  $\text{Ca}(\text{OH})_2$  163 from the  $\text{CaCO}_3$  in stream 158 for use in the causticizing of sodium carbonate at 144. The sodium hydroxide generated during this causticizing causes the conversion of CaS to NaHS. Non-process elements contained in washed calcium carbonate stream 158 are purged 15 at 164 before entering the lime kiln 161. Calcium carbonate 68 required to the gasifier is diverted upstream of the kiln 161. Make-up calcium 70 as  $\text{CaCO}_3$ ,  $\text{CaO}$  or  $\text{Ca}(\text{OH})_2$  is added as required to compensate for calcium lost through purging non-process elements.

20 An alternative process for producing the white liquor for use in the digestion process is illustrated in Figure 4. This involves the production of split white liquor streams, one having a low sulfide content and one having a high sulfide content. These split white liquor streams can then be used for a multistage digestion process. A white liquor stream with a high sulfide content is more desirable at the early 25 stages of delignification, while a white liquor with a lower sulfide content and a higher NaOH concentration is more desirable later in the delignification process to more effectively remove lignin without effecting the pulp fiber strength.

30 In this Figure 4 embodiment, solids 18 containing sodium and calcium compounds plus the non-process elements are discharged from

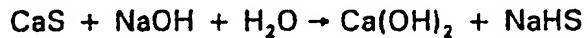
the gasifier into a dissolving tank 72. The following reactions occur in the dissolving tank 72:



5           Sodium compounds are dissolved to form a green liquor. In order to generate two liquor streams of high and low sulfidity, the calcium solids must be separated from the sodium compounds before CaS is converted by reaction with NaOH. Since NaOH is formed in the dissolving tank when Na<sub>2</sub>S is hydrolyzed, some calcium sulfide may

10          begin conversion. If required to slow down the conversion process, the green liquor 78 may be cooled at 165 before entering the solids separation filter 166 where the solid CaS 167 is separated. The solids 167 are discharged into a CaS conversion tank 168 where CaS is converted using NaOH. Most likely, the source of NaOH will be low sulfidity white liquor 170. Water as needed is added at 172. The tank 168 is heated as necessary to a temperature between 80°C and 100°C to promote the following reactions:

15



20          An unclarified high sulfidity white liquor 174 is discharged from the CaS conversion tank 168 to a filter 176 to separate the calcium solids. Discharged from the filter 176 is a clarified high sulfidity white liquor 178 and solids 180 containing mostly CaCO<sub>3</sub>, plus smaller amounts of Ca(OH)<sub>2</sub> and non-process elements. These solids 180, now separated from the high sulfidity white liquor 178 are filtered (washed and dewatered) at 182 with water 184. The liquid 186 which is similar to weak wash is discharged from the filter 182 and recycled back to the dissolving tank 72. Make-up water 74 is added if necessary to this stream 186. The solids 68 discharged from the filter is recycled back to the gasifier with whatever purge 188 may be required as mentioned

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earlier. Make-up calcium 70 is again added to the level required in the gasifier.

A second white liquor stream containing a low sulfidity (low NaHS) concentration is generated from the green liquor stream 190 5 discharged from first solids filter 166. This liquor is high in Na<sub>2</sub>CO<sub>3</sub> and low in Na<sub>2</sub>S. The carbonate must be converted to NaOH. This is done in a conventional causticizing system using the lime kiln 192 and slaker 194 to produce the Ca(OH)<sub>2</sub> stream 196 for the causticizer 198 as more 10 fully described in reference to Figure 2. The liquor 200 from the causticizer 198 is filtered at 202 to give the low sulfidity white liquor stream 204 and the solid CaCO<sub>3</sub> stream 206. A portion 170 of the white liquor 204 is recycled to a CaS conversion tank 168 while the remainder is sent to the pulping process. The solid CaCO<sub>3</sub> stream 206 is washed and filtered at 208 to yield the CaCO<sub>3</sub> stream 210 for the 15 causticizing operation. The wash water 212 from the washer/filler 208 is returned to the dissolving tank 72. As shown, water is supplied to the washer/filter 208 at 214 while water 216 is supplied to the slaker 194.

The invention can also produce a third pulping liquor in the form 20 of sodium sulfite (Na<sub>2</sub>SO<sub>3</sub>). Sulfite is produced from scrubbing SO<sub>2</sub> contained in the flue gas 136 as described previously. The invention not only produces sulfite as a byproduct of gasification, but can also control the quantity of sulfite produced. Sulfur capture in the gasifier is dependent on many factors including temperature, mixing 25 characteristics, gas and particle residence times and ratio of calcium to sulfur (molar basis). For the most part, all of the above factors will be somewhat constant. However, the ratio of calcium to sulfur, also known as the Ca to S mole ratio, can be easily controlled by controlling the feed rate of calcium into the reactor. Reducing the Ca/S mole ratio 30 will reduce sulfur capture as CaS and increase H<sub>2</sub>S production.

Increased H<sub>2</sub>S production and hence increased SO<sub>2</sub> production allows increased production of sulfite in the SO<sub>2</sub> scrubber 138.

Since the recycled calcium compounds in line 68 are moist, some of the heat in the gasifier is used merely to dry the calcium compounds.

5      Therefore, instead of injecting them directly back into the gasifier, they may be injected through line 69 into the hot product gas from the gasifier. For example, they may be injected into the separator 50 as illustrated in Figure 4 such that the hot gases dry the calcium compounds and then separates them from the gases along with other solids for recycle to the gasifier. Alternatively, they could be injected into a dedicated contact device located in line 56 and then separated 10 from the gases for recycle apart from the recycle 52 of the other solids.

**Claims:**

1. A process for the recovery of chemicals from the black liquor generated in a pulp delignification process, said recovery process utilizing a circulating fluidized bed reactor and comprising the  
5 steps of:
  - a. injecting into said fluidized bed reactor and reacting therein said black liquor and substoichiometric reaction air whereby solid  $\text{Na}_2\text{CO}_3$ , solid  $\text{Na}_2\text{S}$  and a gaseous product containing gaseous  $\text{H}_2\text{S}$  are formed;
  - b. injecting a solid calcium compound into said fluidized bed reactor and reacting said calcium compound with said gaseous  $\text{H}_2\text{S}$  to produce solid  $\text{CaS}$  in said fluidized bed reactor;
  - c. discharging solids from said fluidized bed reactor, said  
15 solids containing said solid  $\text{Na}_2\text{CO}_3$ , said solid  $\text{Na}_2\text{S}$  and said solid  $\text{CaS}$ ;
  - d. dissolving said discharged solid  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{S}$  in water to form green liquor containing solid  $\text{CaS}$ ;
  - e. reacting said solid  $\text{CaS}$  with  $\text{NaOH}$  to form  $\text{NaHS}$ ; and
  - 20 f. processing said green liquor and said  $\text{NaHS}$  to form at least one white liquor stream.
2. A process as recited in claim 1 wherein said step (e) of reacting and step (f) of processing comprise the steps of recycling a portion of said white liquor containing  $\text{NaOH}$  to said green liquor  
25 containing solid  $\text{CaS}$  whereby said solid  $\text{CaS}$  is converted to  $\text{NaHS}$  in said green liquor and causticizing said green liquor containing said  $\text{NaHS}$  to form said white liquor stream.
3. A process as recited in claim 1 wherein said calcium compound is selected from the group consisting of  $\text{CaO}$ ,  $\text{CaCO}_3$ ,  $\text{Ca(OH)}_2$ ,  
30 and mixtures thereof.

4. A process as recited in claim 1 wherein said step (e) of reacting CaS with NaOH to form NaHS also forms solid  $\text{Ca(OH)}_2$  and further including the steps of separating said solid  $\text{Ca(OH)}_2$  and recycling said solid  $\text{Ca(OH)}_2$  to said fluidized bed reactor.
5. A process as recited in claim 1 wherein said step (e) of reacting and said step (f) of processing comprise the step of causticizing said green liquor containing solid CaS whereby NaOH is formed and CaS simultaneously reacts with said formed NaOH to form NaHS in said white liquor.
10. A process as recited in claim 5 wherein said calcium compound is selected from the group consisting of  $\text{CaO}$ ,  $\text{CaCO}_3$ ,  $\text{Ca(OH)}_2$  and mixtures thereof.
15. A process as recited in claim 5 wherein said step (e) of reacting CaS with NaOH to form NaHS also forms  $\text{Ca(OH)}_2$  and further including the steps of separating said  $\text{Ca(OH)}_2$  and recycling one portion thereof to said fluidized bed reactor and processing another portion thereof for causticizing said green liquor.
20. A process as recited in claim 1 and further comprising the step of separating said solid CaS from said green liquor prior to step (e) and wherein said step (f) of processing said green liquor comprises the step of causticizing said green liquor with said solid CaS separated out to form a first white liquor and said step (f) of processing said NaHS comprises the step of removing calcium solids and forming a high sulfide second white liquor.
25. A process as recited in claim 8 and further including the step of cooling said green liquor containing said CaS to minimize conversion of CaS prior to separating said CaS from said green liquor.
30. A process as recited in claim 4 wherein said gaseous product with said gaseous  $\text{H}_2\text{S}$  removed is discharged from said fluidized bed reactor and wherein said step of recycling said solid

**Ca(OH)<sub>2</sub>** to said fluidized bed reactor further includes the step of contacting said solid **Ca(OH)<sub>2</sub>** with said discharged gaseous product prior to recycling said solid **Ca(OH)<sub>2</sub>** to said fluidized bed reactor to dry said solid **Ca(OH)<sub>2</sub>**.

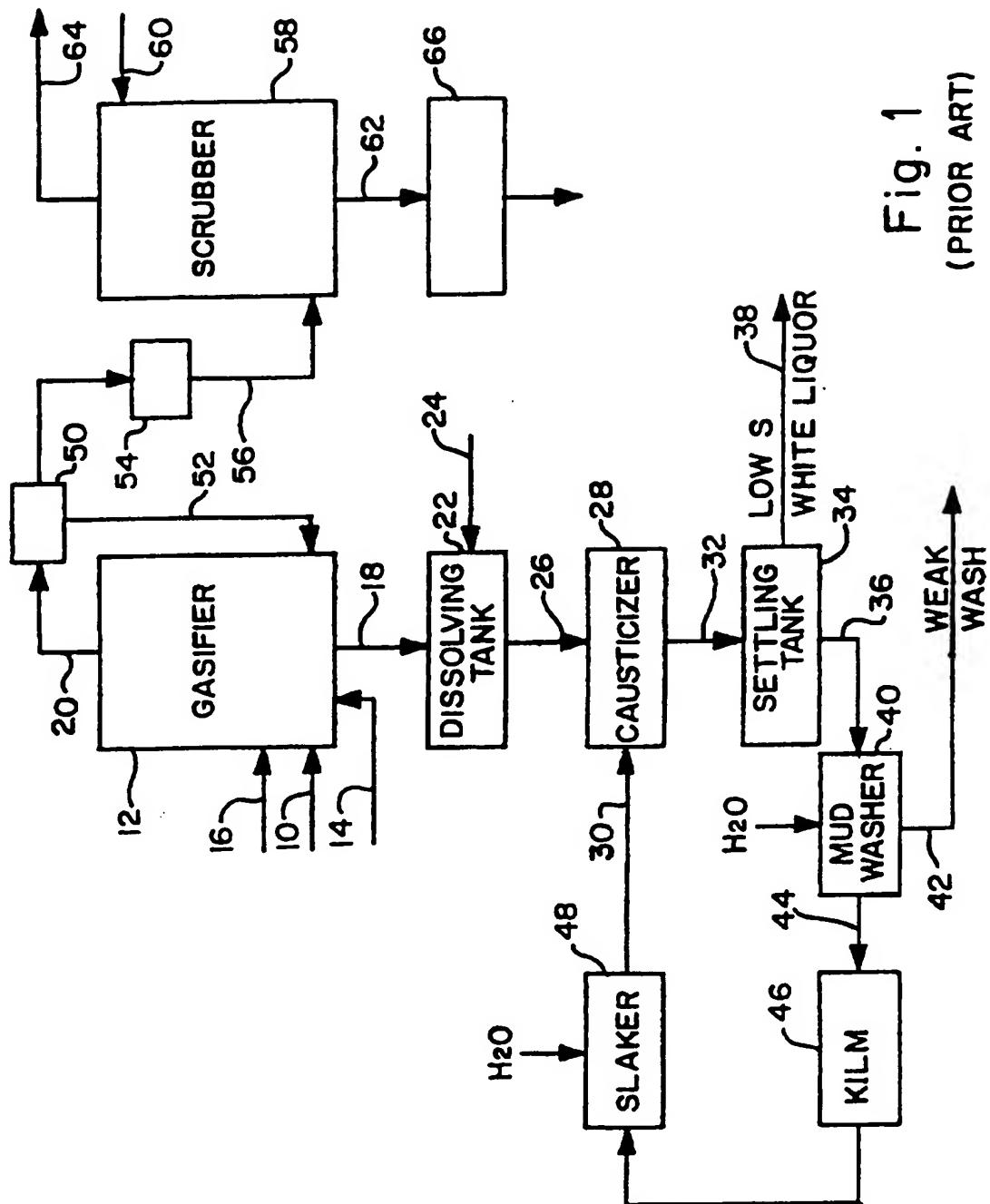


Fig. 1  
(PRIOR ART)

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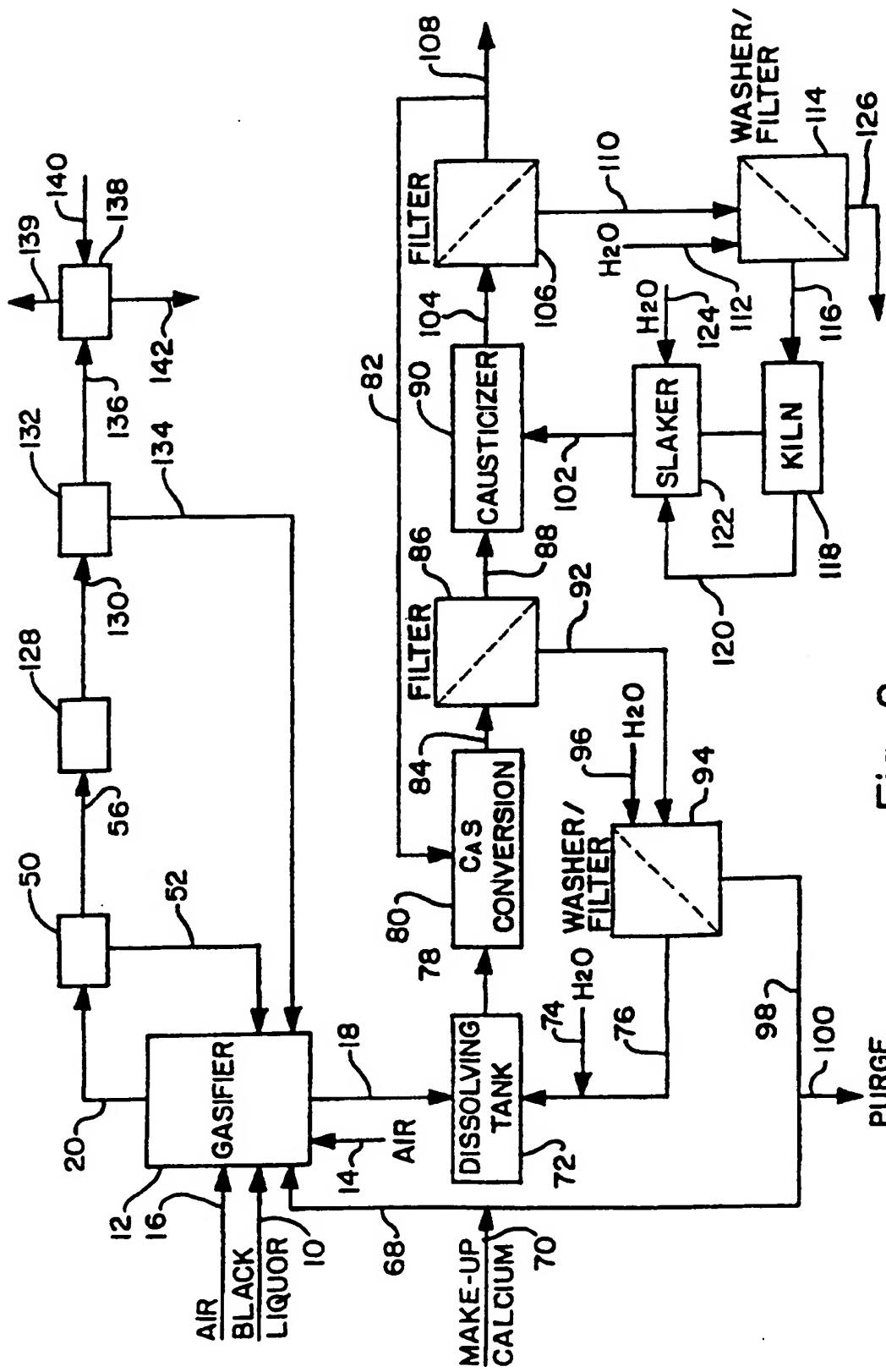


Fig. 2

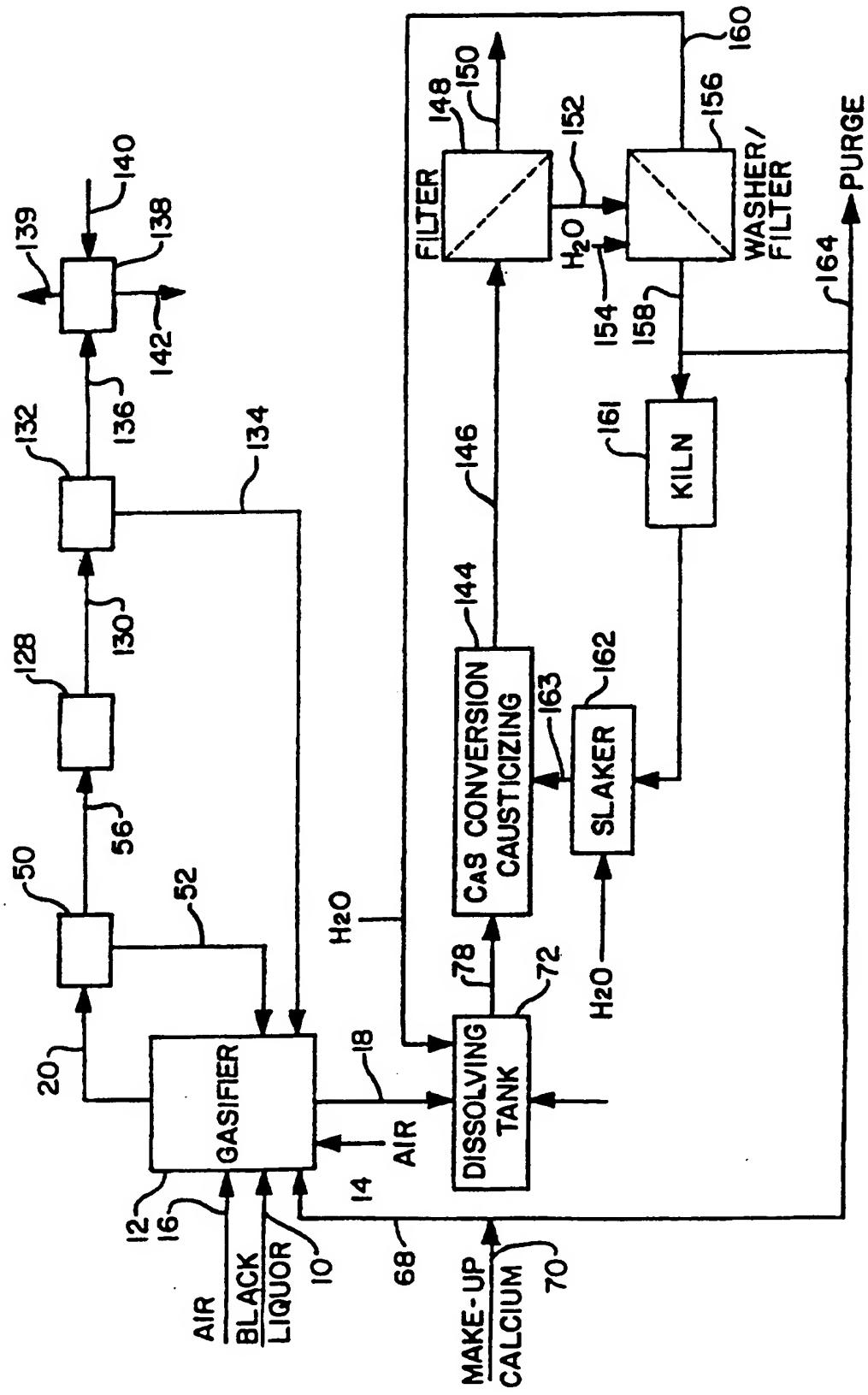
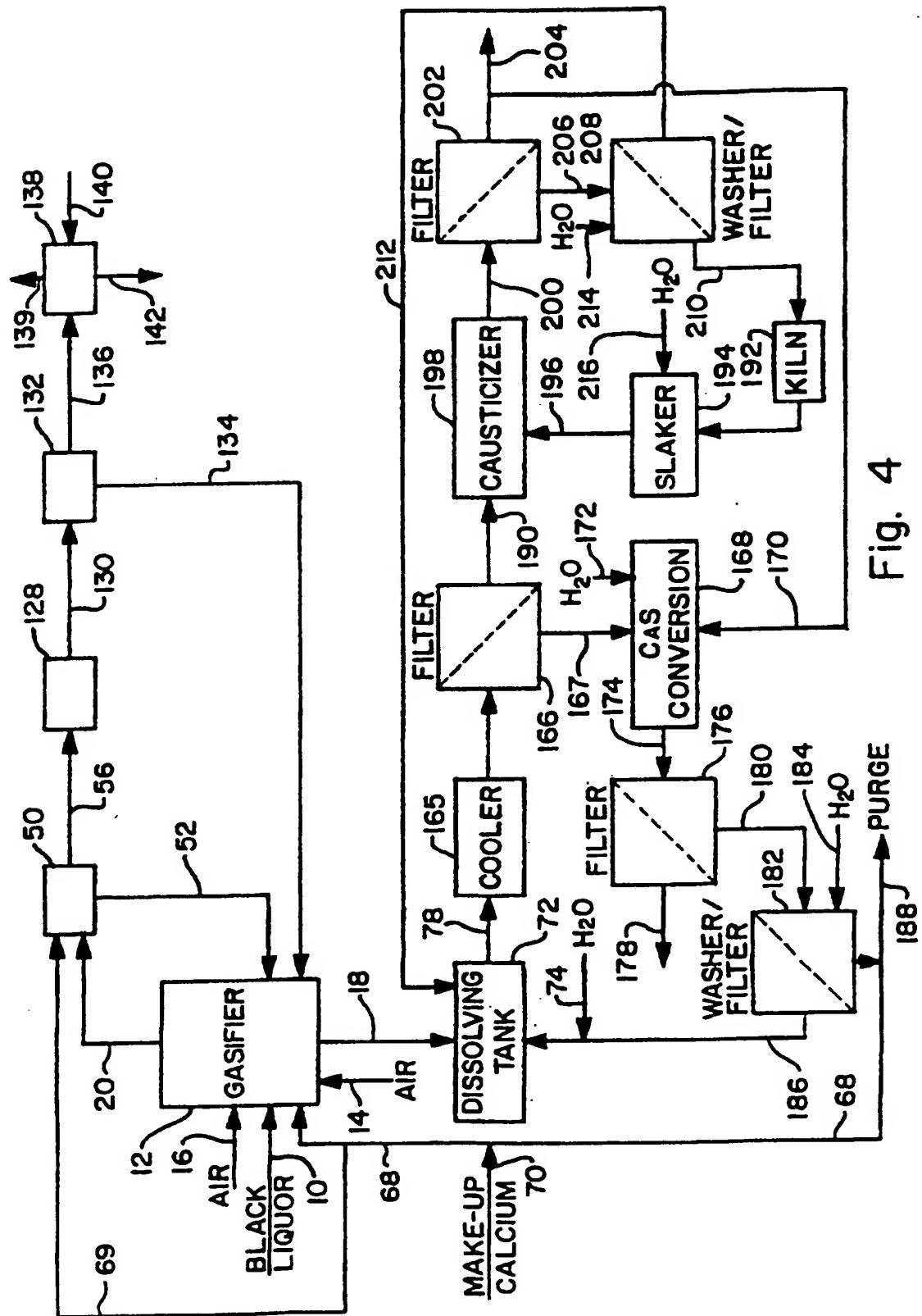


Fig. 3



4  
Fig.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/U- 96/19091

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 D21C11/12 D21C11/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 D21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 94 29516 A (KORSNAES AB) 22 December 1994 see the whole document ---	1-10
Y	US 3 523 864 A (OSTERMAN JOSEPH ET AL) 11 August 1970 see column 5, line 31 - line 38; claims ---	1-10
A	FR 2 550 245 A (NIVELLEAU BRUNIERE PATRICK M F) 8 February 1985 see the whole document ---	1,3-7
A	GB 922 774 A (HANS J. ZIMMER VERFAHRENSTECHNIK) 3 April 1963 see page 2, line 123 - page 3, line 4 -----	1,3



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search

1 April 1997

Date of mailing of the international search report

04.06.97

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 96/19091

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